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## Processing of Clay/Epoxy Nanocomposites with A Three-Roll Mill Machine

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### ABSTRACT

In the present study, a three-roll mill machine was used to disperse/exfoliate the nanoclay particles in an epoxy matrix. The compounding process was carried out with varying mixing time and concentrations of clay particles (1 to 10 wt.%). It was found that the longer the mixing time, the higher the degree of intercalation. Mechanical properties, XRD and TEM were used to characterize the nanocomposites. Elastic modulus was found to increase with increasing clay content, however, the tensile strength was not found to vary accordingly. Compared to conventional direct and solution mixing techniques, the compounding of clay/epoxy nanocomposites by a three-roll mill was found to be highly efficient in achieving higher levels of intercalation/exfoliation in a short period of time and also environmentally friendly.

### INTRODUCTION

Over the last decade, polymer based composites containing nano-scale layered silicate clay particles have drawn significant attention [1-11]. This is mainly because the addition of a small amount of clay particles (<5 wt.%) can show significant improvement in mechanical, thermal and barrier properties of the final composite without requiring special processing techniques. These composites are now being considered for applications ranging from food, electronic, automotive to aerospace industries. It is generally believed that the improvement of properties of nanoclay composites is directly related to the complete exfoliation of silicate layers in the polymer matrix. However, a processing technique that produces complete exfoliation is still a technical challenge. This may be due to the high viscosity of the resin and the strong tendency of nanoclay particles to agglomerate [3]. It is also reported that the degree of exfoliation depends on the structure of clays, curing temperature and curing agent [4]. The commonly used techniques to process clay-epoxy nanocomposites are: direct mixing and solution mixing [4-7]. However, these techniques produce intercalated or intercalated/exfoliated composites rather than exfoliated composites. Vaia et al. have suggested that the degree of exfoliation can be improved through the aid of conventional shear devices such as extruders, mixers, ultrasonicators etc. [8]. In the present study, a three-roll mill machine was used as a means of applying an external shearing force to exfoliate the stacked layers of silicate clay in the epoxy matrix. The correlation between degree of exfoliation and mechanical properties of the nanocomposites is also discussed here.

### EXPERIMENTAL

A diglycidyl ether of bisphenol A (DGEBA) epoxy resin cured with methyl tetrahydrophthalic anhydride hardener from Vantico was used as the matrix. 1-Methylimidazole was used as an accelerator. They were in proportions of 100:90:1 (phr) respectively. The reinforcing nanoclay particle was Nanomer I.28E commercially available from Nanocor, Inc. It

is a natural montmorillonite (MMT) modified with a quaternary amine. It has a surface area of about 750 m<sup>2</sup>/g, an aspect ratio of 200-500 and a platelet thickness of 1 nm [12].

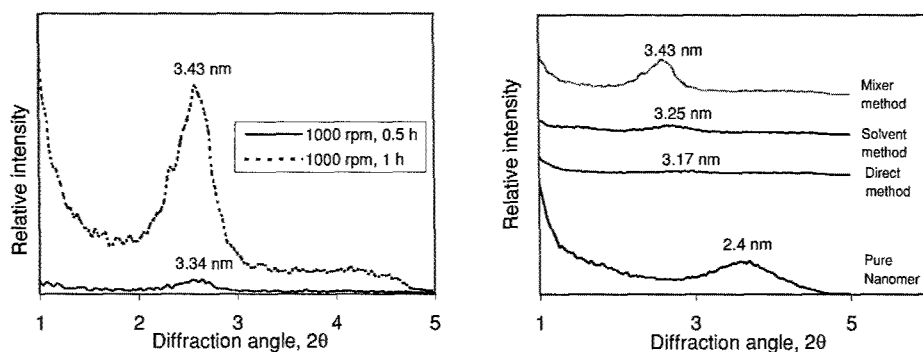
In this study, a three-roll mill machine (Ross Bench Top Model 52M 2.5" x 5") was used to disperse and exfoliate the nanoclay particles in the epoxy matrix. First, the epoxy resin (DGEBA) was placed between the feed and center rolls. Once the rolls started moving, the clay particles were spread gradually on the resin to get direct and maximum contact with the rolls. The dispersion was achieved by the shear forces generated between the adjacent rolls. Compounding was carried out at room temperature for 3 h, with a rotation speed of 500 rpm and a feed rate of 120 g/h. It was observed that the mixture became viscous and opaque as the silicate layers dispersed and expanded with time. However, when the dispersion was completed, it produced a clear and transparent mixture. The final product from the mixer was then collected and mixed with hardener at 60 °C for 1 h on a hot plate. After adding accelerator and mixing for a few minutes, the solution was left overnight for degassing. After degassing, the mixture was poured in an aluminum mold and cured in an oven at 148 °C for 1 h. Nanocomposites were prepared with clay concentrations from 1 to 10 wt.%.

The tensile samples were prepared following ASTM standard D638-99 and tested on an Instron 8500 servohydraulic machine at a crosshead rate of 0.127 mm/min. Small angle X-ray scattering (SAXS) was performed on both clay and uncured nanocomposites, whereas, wide angle X-ray diffraction (WAXD) was performed on cured nanocomposites to evaluate the degree of clay exfoliation. SAXS was carried out on a Bruker AXS solid-state detector with CuK $\alpha$  radiation ( $\lambda = 1.541 \text{ \AA}$ ) and operating at 30 kV and 13 mA. The 2D-diffraction pattern for each sample was collected for 1.5 h. WAXD was carried out on a RIGAKU diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.541 \text{ \AA}$ ) with a scanning speed of 0.5°/min and operating at 40 kV and 20 mA. The degree of exfoliation was further confirmed using a JEOL TEM operating at an accelerating voltage of 100 kV. The ultra-thin TEM sample with a thickness of 60 nm was cut using a microtome at room temperature. The fracture surfaces of tensile specimens were examined using a Hitachi S4500 FE scanning electron microscope. The fracture surfaces were gold coated prior to SEM investigation to avoid charging and were examined at 3 kV accelerating voltage.

## RESULTS AND DISCUSSION

Figure 1a shows the SAXS patterns of 3 wt.% clay nanocomposites prepared using the mixer at 1000 rpm. The patterns reveal the effect of mixing time on intercalation. The stronger peak obtained after 1 h mixing compared to 0.5 h mixing implies that an ordered intercalated nanocomposite was formed. This also indicates that an optimum balance between residence time and level of shear is required to facilitate the intercalation/exfoliation and dispersion of layered silicates. The pure Nanomer shows a characteristic diffraction peak corresponding to the (001) plane at 2.4 nm (figure 1b). The increase in d-spacing from 2.4 to 3.34 nm (~40% higher) after mixing just for 0.5 h indicates that the mixer is highly efficient in making an intercalated nanocomposite within a short period of time.

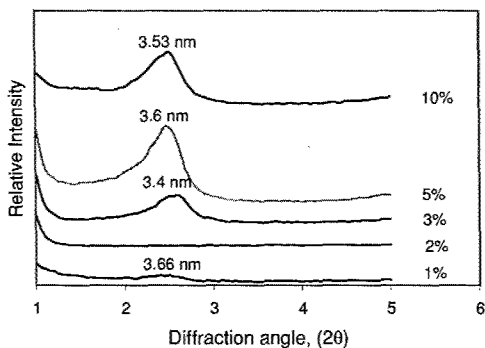
In earlier investigations [13], nanocomposites were also prepared using both direct and solution methods. In the direct method, clays were mixed in an epoxy resin at 60 °C for 3 h using a magnetic stirrer and a hot plate. In the solution method, clays were dissolved in acetone for 3 h using an ultrasonic bath prior to mixing in an epoxy resin. Figure 1b shows a comparison in SAXS patterns of 3 wt.% nanocomposites under all processing methods. Both direct and solution methods show weaker peaks as well as lower d-spacing (3.17 and 3.25 nm respectively)



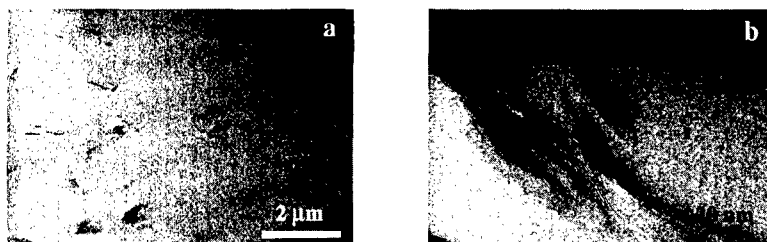
**Figure 1.** SAXS patterns of 3 wt.% clay nanocomposites. (a) Effect of mixing time (b) Effect of processing techniques.

compared to the mixer method (3.43 nm). It is thus clear that the shear force between adjacent rolls acts as a driving force to disperse and intercalate the clay platelets, whereas, no such shear effect is present in other methods. Furthermore, as the mixing time increases the viscosity of the mixture increases, which in turn may provide an extra shear force to disperse the clay platelets [11]. Therefore, it can be suggested that the mixer produces a good intercalated nanocomposite in a more efficient way compared to both direct and solution methods.

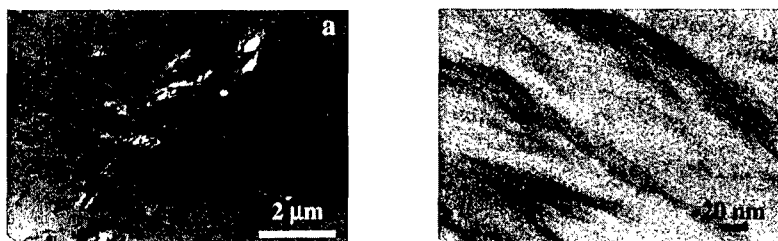
Figure 2 shows the WAXD patterns of nanocomposites containing 1 to 10 wt.% of clay prepared using the mixer for 3 h at 500 rpm. The nanocomposite with 1 wt.% clay shows a shallow peak with d-spacing of 3.66 nm, whereas, the nanocomposite with 2 wt.% of clay shows no peak which is indicative of an exfoliated structure. Since the viscosity of 2 wt.% clay nanocomposite is higher than that of 1 wt.% clay, the extra shear force in the former case may cause better exfoliation of clay platelets in the epoxy resin as suggested elsewhere [11]. However, the nanocomposites with higher clay content (>2 wt.%) show pronounced peaks from silicate basal planes ( $d_{001}$ ) with d-spacing slightly lower than the composite containing 1 wt.% of clay. Therefore, the absence of peak in the case of 2 wt.% clay nanocomposite needs further confirmation by SAXS or low speed WAXD patterns. In general, the lower d-spacing at higher



**Figure 2.** WAXD patterns of nanocomposites with varying clay contents.



**Figure 3.** TEM images of 1 wt.% clay nanocomposite. (a) Low mag.: (b) high mag.

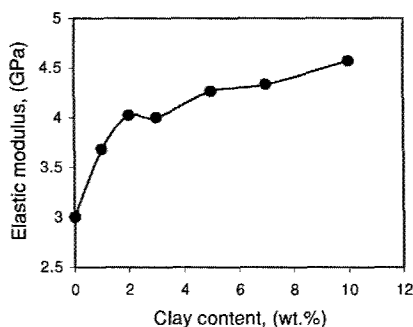


**Figure 4.** TEM images of 10 wt.% clay nanocomposite. (a) Low mag.: (b) high mag.

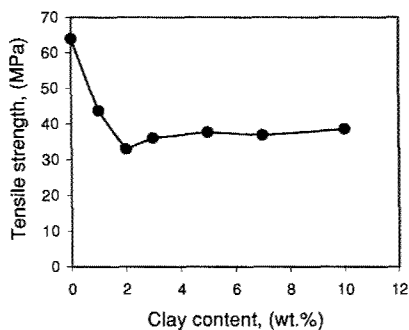
clay content is attributed to the increased intercalating sites with increased clay content that might impede the exfoliation of individual silicate layers [9]. Therefore, it can be suggested that the 2 wt.% clay nanocomposite shows complete exfoliation with respect to the shear force and residence time applied in this study, whereas, the addition of higher clay content produces ordered intercalated nanocomposite. It is of interest to mention that the compounding of Cloiste 30B (Southern Clay Products Inc.) in the same epoxy matrix and identical conditions shows complete exfoliation regardless of clay content [13]. This indicates that the degree of exfoliation depends on the type of clay and its surface modification.

The TEM images of nanocomposites containing 1 and 10 wt.% of clay are presented in figures 3 and 4 respectively. The dark lines in figures 3b and 4b are the intersections of silicate layers of 1 nm thick. Both composites show intercalated structures with an average distance between two platelets of 3.6 nm and therefore, in good agreement with the WAXD results (figure 2). Figure 4a shows nano voids inside the silicate clay layers and this is an indication of improper degassing due to high viscosity of the mixture at high clay concentrations.

The variation of elastic modulus with the percentage of clay content is shown in figure 5. It is found that the modulus of the composite increases continuously with increasing concentration of clay. An improvement of about 34% is observed just for an addition of 2 wt.% of clay. However, the improvement of only 42 and 52% for an addition of 5 and 10 wt.% of clay respectively, signifies that the rate of improvement decreases at higher concentrations. The improvement in elastic modulus can be attributed to the well dispersion of nano-size clay particles as well as to the good interfacial adhesion between the particles and the epoxy matrix [3]. Therefore, the clay particles will restrict the mobility of polymer chains under loading. The orientation of silicate



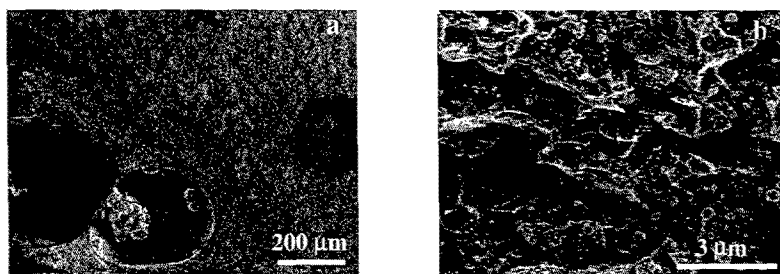
**Figure 5.** Effect of clay content on elastic modulus of clay/epoxy nanocomposites.



**Figure 6.** Effect of clay content on tensile strength of clay/epoxy nanocomposites.

layers and polymer chains with respect to the loading direction can also contribute to the reinforcement effects [10]. However, the decreasing rate of elastic modulus improvement with higher clay content can be attributed to the presence of unexfoliated aggregates [10].

Figure 6 shows the variation in tensile strength with the percentage of clay content. Unlike the elastic modulus, nanocomposites with any clay concentration show a lower tensile strength than the pure epoxy. This is similar to the results reported by Zerda et al [5] but in contrast to the tensile strength values of nanocomposites reported elsewhere [3,10,11]. However, the failure of all nanocomposites at strengths lower than the pure epoxy can be assumed to be compounding process related. As mentioned before, the compounding process of nanoclay in an epoxy matrix with a three-roll mill produces a highly viscous and foamy material, and the higher the clay content the higher the viscosity. The Nanomer particles treated with ammonium ions also accelerate the curing process of epoxy resin [12]. Therefore, the mixture becomes highly viscous with time and hinders the complete degassing before casting. It is also observed that the degassing problem becomes critical for nanocomposites containing more than 5 wt.% of clay, which in turn, produces nanocomposites with nano to micro-level voids. The presence of nano-voids in 10 wt.% clay nanocomposites (figure 4a) confirms this. The other source of voids could be trapped air during pouring of highly viscous material onto the mold. The failure of all specimens at the same strength level (30 to 40 MPa) also indicates the possibility of crack



**Figure 7.** SEM fractographs of 10 wt.% clay nanocomposite.  
(a) Crack initiation from voids (b) Fracture surface at higher magnification

initiation from similar type of defects. Therefore under tensile loading, cracks should initiate from these tiny voids and cause the specimen to fail at relatively low strain. Figure 7a confirms the crack initiation from such micro-voids during tensile testing of a 10 wt.% clay/epoxy nanocomposite. Figure 7b shows the same fracture surface at higher magnification. The bright spots correspond to clay aggregates and finely dispersed in the material. This observation further confirms the incomplete exfoliation or inevitable aggregation of clay layers in this nanocomposite. The presence of such clay aggregates in the microstructure of nanocomposite is also reported by Kornmann et al. [7]. These loose clusters or unexfoliated nanoparticles in the matrix may act as additional crack initiation sites by splitting up easily under applied load [5]. A better degassing and exfoliation technique is, therefore, very important and is now under investigation to improve the tensile strength of clay/epoxy nanocomposites.

## CONCLUSIONS

The compounding of nanoclay composites with a three-roll mill machine is found to be highly appealing and environmentally friendly since no solvent is required. Compared to direct and solution methods, the mixer is found highly efficient in achieving a higher degree of intercalation/exfoliation within a short period of time. It is also found that the longer the mixing time, the higher the degree of intercalation. The complete exfoliation in 2 wt.% clay nanocomposite indicates that an optimum balance between clay content, residence time and level of shear is required to facilitate the exfoliation and dispersion of layered silicates. The elastic modulus of the composites is found to increase with increasing concentration of clay content. The highest rate of improvement in modulus in 2 wt.% clay nanocomposite confirms the direct relation between degree of exfoliation and mechanical properties in such systems. However, the apparent lower tensile strength of the nanocomposites with respect to pure epoxy can be attributed to the clustering of nanoparticles as well as to the nano to micro-size voids in the microstructure generated due to inadequate degassing of the mixture.

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